

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平8-131841

(43) 公開日 平成8年(1996)5月28日

(51) Int.Cl. <sup>8</sup>	識別記号	庁内整理番号	F I	技術表示箇所
B 0 1 J	35/02	J		
	21/06	M		
	37/02	3 0 1 C		

審査請求 未請求 請求項の数3 書面 (全 4 頁)

(21) 出願番号 特願平6-312310

(22) 出願日 平成6年(1994)11月10日

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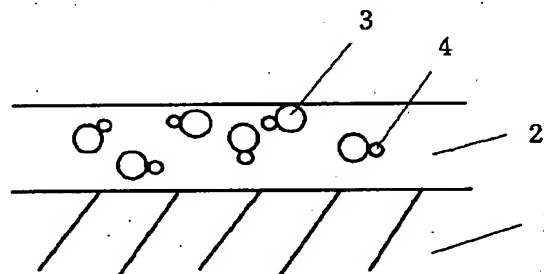
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(54) 【発明の名称】 光触媒作用を有する部材

(57) 【要約】

【目的】 300℃未満の低温の熱処理でも良好な光触媒活性を有する部材を作製でき、基材表面に汚れが付きにくく、なおかつ基材表面に光触媒活性と撥水性等の他の機能を共存させ得る部材構造を提供すること。

【構成】 基材表面に金属粒子を光還元法により固定した光触媒粒子と光触媒活性耐蝕性バインダーとの混合層よりなる薄膜が形成されているようにする。



【特許請求の範囲】

【請求項1】 基材表面に金属粒子を光還元法により固定した光触媒粒子と光触媒活性耐蝕性バインダーとの混合層よりなる薄膜が形成されていることを特徴とする光触媒作用を有する部材。

【請求項2】 前記光触媒活性耐蝕性バインダーは、撥水性を有することを特徴とする請求項1に記載の光触媒作用を有する部材。

【請求項3】 前記光触媒活性耐蝕性バインダーは、釉薬であることを特徴とする請求項1に記載の光触媒作用を有する部材。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、タイル、ガラス（鏡）、衛生陶器、化粧合板等の基材の表面に、抗菌性、防汚性、脱臭性や $\text{NO}_x$ 等の有害物質を分解する機能を有する部材に関する。

【0002】

【従来技術】基材の表面に、抗菌性、防汚性および脱臭性等の機能を付加する方法として、従来より基材表面にアナターゼ $\text{TiO}_2$ 等の光触媒の薄膜を形成する方法が提案されている。

【0003】その1つの方法としてアナターゼ型 $\text{TiO}_2$ 粒子をバインダーに混練し、これを基材表面に塗布して熱処理する方法が知られている。他の方法として、本出願人が特開平5-253544号において開示した、居住空間の壁面、床面或いは天井面を構成する板状部材の表面にバインダ層を形成し、このバインダ層の表面にアナターゼ型 $\text{TiO}_2$ を主体とする光触媒微粉末をその一部がバインダ層から露出するように吹き付けて付着させ、次いで300℃以上900℃未満の範囲で加熱してバインダ層を熔融せしめた後、冷却してバインダ層を固化せしめるようにしたことを特徴とする脱臭機能を備えた板状部材の製造方法がある。

【0004】

【発明が解決すべき課題】アナターゼ型 $\text{TiO}_2$ 粒子をバインダーに混練しこれを基材表面に塗布して熱処理する方法では、光触媒の活性なサイトをバインダーが覆ってしまうため脱臭性等の光触媒作用による特性が充分でなかった。また、特開平5-253544号の方法では、300℃以上900℃未満で熱処理すれば脱臭性等が良好だが、300℃未満の低温で良好な脱臭特性が得られなかった。したがって耐熱性のないプラスチック等の基材に優れた脱臭特性等の良好な光触媒活性を付加することは困難であった。その理由として基材に光触媒粒子を塗布する前工程において光触媒微粒子を懸濁液中に単分散させる必要があるがそのために有機系の分散剤を添加しており、その分散剤が300℃未満では充分に分解蒸発せず、光触媒粒子上の活性なサイトを覆うように残留しているためと考えられる。

【0005】また、特開平5-253544号の方法では、800℃未満の温度では基材表面を形成する光触媒層が気孔率40%以上の多孔質であり、そのため汚れが付きやすい傾向があった。また抗菌性、防汚性の観点からいえば、基材表面は撥水性を有することが望ましいが、光触媒粒子を撥水性を有する樹脂と混練して基材表面に塗布熱処理する方法では、基材表面は一層撥水性を有する粒子で覆われるために撥水性はあるが、やはり撥水性樹脂により光触媒粒子上の活性なサイトが覆われてしまうために光触媒活性は有しなかった。

【0006】本発明は以上の事情を鑑みてなされたものであり、300℃未満の低温の熱処理でも良好な光触媒活性を有する部材を作製でき、基材表面に汚れが付きにくく、なおかつ基材表面に光触媒活性と撥水性等の他の機能を共存させ得る部材構造を提供することを目的とする。

【0007】

【課題を解決するための手段】本発明では上記課題を解決すべく、光触媒作用を有する部材において基材表面に金属粒子を光還元法により固定した光触媒粒子と光触媒活性耐蝕性バインダーとの混合層よりなる薄膜が形成されているようにした。

【0008】ここで基材の材質は、陶磁器、セラミックス、金属、ガラス、熱硬化性樹脂、熱可塑性樹脂あるいはその複合物等基本的に何でもよい。基材の形状もどのようなものでもよく、球状物、円柱物、円筒物やタイル、壁材、床材等の板状物などの単純形状のものでも、衛生陶器、洗面台、浴槽、流し台などの複雑形状のものでも構わない。また、基材表面は、多孔質でも緻密質でもよい。

【0009】金属粒子とは、光触媒粒子に担持した場合、光触媒粒子に光が照射され電子と正孔が生成したときに電子を捕捉しうる金属粒子をいい、具体的にはAg、Cu、Pt、Pd、Ni、Co、Fe等をいう。光還元法による固定とは、金属塩水溶液中に光触媒粒子を入れ、紫外線を含む光を照射して光触媒粒子に金属を固定させる方法をいう。

【0010】光触媒粒子とは、防臭機能、抗菌機能等を発揮するのに充分なバンド・ギャップを有する半導体粒子のことである。光触媒粒子が抗菌機能を有する理由としては所定以上の電圧が印加されることにより感電死するという説（特公平4-29393）もあるが、一般には防臭特性と同様に、光照射時に生じる活性酸素のためと考えられている。活性酸素を生成するためには、半導体の伝導帯の位置がバンドモデルで表すとき水素発生電位より上方にあり、かつ価電子帯の上端が酸素発生電位より下方にあることを要する。この条件を満たす半導体には、 $\text{TiO}_2$ 、 $\text{SrTiO}_3$ 、 $\text{ZnO}$ 、 $\text{SiC}$ 、 $\text{GaP}$ 、 $\text{CdS}$ 、 $\text{CdSe}$ 、 $\text{MoS}_3$ 等がある。また微粒化すると伝導帯の位置は上方に移動するので、1~10nm

m程度の微粒子ならば、 $\text{SnO}_2$ 、 $\text{WO}_3$ 、 $\text{Fe}_2\text{O}_3$ 、 $\text{Bi}_2\text{O}_3$ 等も活性酸素を生成しうる可能性がある。このうち化学的に安定で、安価に活性の高い微粒子を得ることができることから、アナターゼ型 $\text{TiO}_2$ が特に好ましい。

【0011】金属粒子を光還元法により固定した光触媒粒子の作製方法は以下に示す方法で行う。まず、光触媒ゾル溶液を作製する。光触媒ゾルはなるべく単分散させる。例えばアナターゼ型 $\text{TiO}_2$ の場合には等電点が $\text{pH} 6.5$ なので酸性またはアルカリ性で分散させる。この際、分散性を向上させるために分散剤（解膠剤）や表面活性剤若しくは表面処理剤を添加してもよい。光触媒ゾル溶液に用いる溶媒は基本的に何でもよい。一般的には水やエタノールがよく使用される。

【0012】次に光触媒ゾル溶液とほぼ同じ $\text{pH}$ に調整した金属溶液を光触媒ゾル溶液に添加する。ここで金属溶液の $\text{pH}$ を光触媒ゾル溶液とほぼ同じにするのは、光触媒ゾルの溶液中のゼータ電位をなるべく変化させないようにすることにより、光触媒ゾルの単分散性を維持するためである。ここで金属溶液とは光触媒粒子に光が照射され電子と正孔が生成したときに電子を捕捉しうる金属を含む塩と溶媒からなる溶液をいい、より具体的には $\text{Ag}$ 、 $\text{Cu}$ 、 $\text{Pt}$ 、 $\text{Pd}$ 、 $\text{Ni}$ 、 $\text{Co}$ 、 $\text{Fe}$ 等を含む塩と溶媒からなる溶液をいう。 $\text{Ag}$ 、 $\text{Cu}$ 、 $\text{Pt}$ 、 $\text{Pd}$ 、 $\text{Ni}$ 、 $\text{Co}$ 、 $\text{Fe}$ 等を含む塩としては硝酸銀、酢酸銅、炭酸銅、硫酸銅、塩化第一銅、塩化第二銅、塩化白金酸、塩化パラジウム、塩化ニッケル、塩化コバルト、塩化第一鉄、塩化第二鉄などが挙げられる。また溶媒としては水、エタノール、プロパノール等が使用できるが、なるべく光触媒ゾルと同じ種類を用いることが望ましい。

【0013】次に光触媒ゾル溶液と金属塩溶液とを攪拌しながら紫外線を含む光を照射する。ここで紫外線を含む光を照射する光源は、紫外線を含む光を照射しうるものであればよく、具体的には紫外線ランプ、BLBランプ、キセノンランプ、水銀灯、蛍光灯などが挙げられる。紫外線を含む光の照射方法も基本的には問わないが、第一に容器上方から照射するほうがよい。容器による紫外線の吸収がないからである。第二に光源と容器との距離は数cm～数10cm程度がよい。近すぎると光源から発する熱により試料溶液の上面が乾くおそれがあり、遠すぎると照度が低下するからである。照射時間は光源の照度により異なるが数秒～数10分程度照射すれば金属が光触媒粒子に強固に付着する。

【0014】光触媒活性耐蝕性バインダーとは、光触媒反応により分解、変質されにくいバインダーのことをいい、シロキサン樹脂、シリコン樹脂、フッ素樹脂、釉薬、ケイ酸ガラス等がその代表的なものである。ここで用いる光触媒活性耐蝕性バインダーは、混合層中において大部分の光触媒粒子を覆うので、基材表面の光触媒活

性を良好なものにするためには透光性を有したほうがよい。尚、汚れが付きにくい点を考慮すると、バインダーは、シロキサン樹脂、フッ素樹脂等の撥水性を有するものが、望ましい。

#### 【0015】

【作用】光触媒粒子の活性なサイトを予め $\text{Ag}$ 、 $\text{Cu}$ 、 $\text{Pt}$ 、 $\text{Pd}$ 、 $\text{Ni}$ 、 $\text{Co}$ 、 $\text{Fe}$ 等の金属粒子で覆っているので、光触媒活性耐蝕性バインダーとの混練時に光触媒活性耐蝕性バインダーにより光触媒粒子の活性なサイトが覆われることがなく、混合層を形成したときに金属粒子の補足効果により良好な光触媒活性が維持されると共に多くの光触媒粒子は光触媒活性耐蝕性バインダー中に埋もれてしまうため、基材表面が比較的平滑であり、光触媒粒子が基材最表面に露出している場合と比較して、汚れが付きにくい。

#### 【0016】

##### 【実施例】

（実施例1）10cm角のアルミナ基材に撥水性を有するシロキサン・クリア・コート樹脂をプロパノールで希釈した後、硬化剤を添加した溶液を塗布し、さらにその上に結晶径 $0.01\mu\text{m}$ の $\text{TiO}_2$ ゾルの硝酸分散液（ $\text{pH} 0.8$ ）に硝酸で $\text{pH}$ を調整し、 $\text{pH}$ 約 $0.8$ とした酢酸銅水溶液を添加し、溶液上方約8cmの位置に4ワットのBLBランプからなる光源を配置して15分光照射して $\text{TiO}_2$ に銅を担持させた後、撥水性を有するシロキサン・クリア・コート樹脂を $\text{TiO}_2$ ゾルの固形分の約20重量%添加し、さらに希釈剤のプロパノールと硬化剤を順次添加して得た塗布剤を塗布し、150℃で熱処理して図1に示すような試料を得た。図1において、1は基材、2はシロキサン・クリア・コート樹脂（光触媒活性耐蝕性バインダー）、3は $\text{TiO}_2$ 粒子（光触媒粒子）、4は銅粒子（金属粒子）を示すものである。得られた試料について光照射時の防臭特性 $\text{R}30$ （L）および耐摩耗性について評価した。

【0017】光照射時の防臭特性 $\text{R}30$ （L）は、11Lのガラス容器内に試料面を光源（BLB蛍光灯4W）から8cmの距離に配置し、メチルメルカプタンガスを初期濃度3ppmとなるように容器内に注入し、30分光照射した後の濃度変化率である。耐摩耗性については、プラスチック消しゴムを用いた摺動摩耗を行い、外觀の変化を比較し評価した。評価基準を下記に示す。

◎：40回往復に対して変化なし

○：10回以上40回未満の摺動で傷が入り、光触媒を含む層が剥離

△：5回以上10回未満の摺動で傷が入り、光触媒を含む層が剥離

×：5回未満の摺動で傷が入り、光触媒を含む層が剥離

【0018】その結果、防臭特性は $\text{R}30$ （L）=80%、耐摩耗性も◎と良好な結果を示した。さらに接触角測定器により基材表面に滴下した水のぬれ角を測定した

結果73%とかなり高い値を示し、撥水性があることが確認された。この高いぬれ性は基材表面の大部分が撥水性樹脂で覆われているためと解される。

【0019】(比較例1) 10cm角のアルミナ基材に撥水性を有するシロキサン・クリア・コート樹脂をプロパノールで希釈した後、硬化剤を添加した溶液を塗布し、さらにその上に結晶径0.01 $\mu$ mのTiO<sub>2</sub>ゾルの硝酸分散液(PH0.8)に撥水性を有するシロキサン・クリア・コート樹脂をTiO<sub>2</sub>ゾルの固形分の約20重量%添加しさらに希釈剤のプロパノールと硬化剤を順次添加して得た塗布剤を塗布し、150℃で熱処理して試料を得た。得られた試料について光照射時の防臭特性R30(L)および耐摩耗性について評価した。

【0020】その結果、耐摩耗性は◎と良好な結果を示したが、防臭特性はR30(L)=18%と光照射しているにもかかわらず、防臭特性はよくなかった。さらに接触角測定器により基材表面に滴下した水のぬれ角を測定した結果66%とかなり高い値を示し、撥水性があることが確認された。この高いぬれ性は基材表面の大部分が撥水性樹脂で覆われているためと解される。

【0021】(実施例2) 15cm角のタイル基材表面にSiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-PbOフリット(軟化点540℃)を塗布して680℃で焼成後、結晶径0.01 $\mu$ mのTiO<sub>2</sub>ゾルの硝酸分散液(PH0.8)に硝酸でPHを調整しPH約0.8とした硫酸銅水溶液を添加し溶液上方約8cmの位置に4ワットのBLBランプからなる光源を配置して15分光照射してTiO<sub>2</sub>に銅を担持させた金属担持光触媒ゾルと、SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-PbOフリットの混練物を塗布し、680℃で焼成して試料を得た。得られた試料について光照射時の防臭特性R30(L)、耐摩耗性および汚れの付きにくさについて評価した。

【0022】汚れの付きにくさの評価は、基材表面に黒

色の太いマジックインクで線を引き、乾燥後エタノールでインクを拭き取った後の汚れ具合で評価した。評価指標を示す。

◎：完全に跡が消える

○：かすかに跡が残る

△：灰青色の跡が残る

×：黒色の跡が残る

その結果、R30(L)は82%、耐摩耗性は◎、汚れの付きにくさも○と良好な結果を示した。

【0023】(比較例2) 15cm角のタイル基材表面にSiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-PbOフリット(軟化点540℃)を塗布後、さらにその上に結晶径0.01 $\mu$ mのTiO<sub>2</sub>ゾルの硝酸分散液(PH0.8)を塗布し、680℃で焼成して試料を得た。得られた試料について光照射時の防臭特性R30(L)、耐摩耗性および汚れの付きにくさについて評価した。その結果、R30(L)は92%、耐摩耗性は○と良好な結果を示したが、汚れの付きにくさは×であった。

【0024】

【発明の効果】基材表面に金属粒子を光還元法により固定した光触媒粒子と光触媒活性耐蝕性バインダーとの混合層よりなる薄膜が形成されているようにすることにより、300℃未満の低温の熱処理でも良好な光触媒活性を有する部材を作製でき、基材表面に汚れが付きにくく、耐摩耗性が良好でなおかつ基材表面に光触媒活性と撥水性等の他の機能を共存させ得る部材構造を提供することができる。

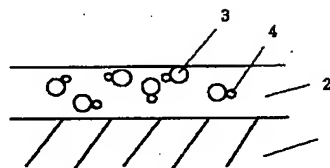
【図面の簡単な説明】

【図1】本発明の実施例を示す図。

【符号の説明】

1…基材、2…光触媒活性耐蝕性バインダー、3…光触媒粒子、4…金属粒子

【図1】



【公報種別】特許法第17条の2の規定による補正の掲載  
【部門区分】第2部門第1区分  
【発行日】平成12年12月5日(2000.12.5)

【公開番号】特開平8-131841  
【公開日】平成8年5月28日(1996.5.28)  
【年通号数】公開特許公報8-1319  
【出願番号】特願平6-312310  
【国際特許分類第7版】

B01J 35/02  
21/06  
37/02 301

【F I】

B01J 35/02 J  
21/06 M  
37/02 301 C

【手続補正書】

【提出日】平成11年4月7日(1999.4.7)

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】特許請求の範囲

【補正方法】変更

【補正内容】

【特許請求の範囲】

【請求項1】 基材表面に金属粒子を光還元法により固定した光触媒粒子と光触媒活性耐蝕性バインダーとの混合層よりなる薄膜が形成されていることを特徴とする光触媒作用を有する部材。

【請求項2】 前記バインダーは、透光性を有することを特徴とする請求項1に記載の光触媒作用を有する部材。

【請求項3】 前記バインダーは、撥水性を有することを特徴とする請求項1又は2に記載の光触媒作用を有する部材。

【請求項4】 前記バインダーは、シロキサン樹脂であることを特徴とする請求項1～3に記載の光触媒作用を有する部材。

【請求項5】 前記バインダーは、フッ素樹脂であることを特徴とする請求項1～3に記載の光触媒作用を有する部材。

【請求項6】 前記バインダーは、ケイ酸ガラスであることを特徴とする請求項1又は2に記載の光触媒作用を有する部材。

【請求項7】 前記バインダーは、釉薬であることを特徴とする請求項1又は2に記載の光触媒作用を有する部材。

【請求項8】 前記金属粒子は、Ag、Cu、Pt、Pd、Ni、Co、Feの群から選ばれる少なくとも1種以上であることを特徴とする請求項1～7に記載の光触

媒作用を有する部材。

【請求項9】 基材表面に金属粒子を光還元法により固定した光触媒粒子と光触媒活性耐蝕性バインダーとからなることを特徴とする光触媒薄膜形成用組成物。

【請求項10】 前記バインダーは、撥水性を有することを特徴とする請求項9に記載の光触媒薄膜形成用組成物。

【請求項11】 前記バインダーは、シロキサン樹脂であることを特徴とする請求項9又は10に記載の光触媒薄膜形成用組成物。

【請求項12】 前記バインダーは、フッ素樹脂であることを特徴とする請求項9又は10に記載の光触媒薄膜形成用組成物。

【請求項13】 前記バインダーは、ケイ酸ガラスであることを特徴とする請求項9に記載の光触媒薄膜形成用組成物。

【請求項14】 前記バインダーは、釉薬であることを特徴とする請求項9に記載の光触媒薄膜形成用組成物。

【請求項15】 前記金属粒子は、Ag、Cu、Pt、Pd、Ni、Co、Feの群から選ばれる少なくとも1種以上であることを特徴とする請求項9～14に記載の光触媒薄膜形成用組成物。

【請求項16】 基材表面に金属粒子を光還元法により固定した光触媒粒子と光触媒活性耐蝕性バインダーとの混合層よりなる薄膜を形成する工程、300℃未満の低温で熱処理する工程を含むことを特徴とする光触媒作用を有する部材の製造方法。

【請求項17】 前記金属粒子は、Ag、Cu、Pt、Pd、Ni、Co、Feの群から選ばれる少なくとも1種以上であることを特徴とする請求項16に記載の光触媒作用を有する部材の製造方法。

【請求項18】 光触媒活性耐蝕性バインダーと混合し

て用いることにより基材の表面に光触媒薄膜を形成させるための光触媒粒子であって、前記光触媒粒子表面には金属粒子が光還元法により固定されていることを特徴とする光触媒粒子。

【請求項19】 前記金属粒子は、Ag、Cu、Pt、Pd、Ni、Co、Feの群から選ばれる少なくとも1種以上であることを特徴とする請求項18に記載の光触媒粒子。

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】発明の名称

【補正方法】変更

【補正内容】

【発明の名称】光触媒作用を有する部材、光触媒薄膜形

成用組成物、光触媒作用を有する部材の製造方法並びに光触媒粒子

【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0001

【補正方法】変更

【補正内容】

【0001】

【産業上の利用分野】本発明は、タイル、ガラス

(鏡)、衛生陶器、化粧合板等の基材の表面に、抗菌性、防汚性、脱臭性やNO<sub>x</sub>等の有害物質を分解する機能を有する部材、前記部材を形成するための光触媒薄膜形成用組成物及び光触媒粒子、並びに前記部材の製造方法に関する。

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## CLAIMS

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[Claim 1] The member which has the photocatalyst operation characterized by forming in a base material front face the thin film which consists of a mixture of the photocatalyst particle and photocatalyst activity corrosion resistance binder which fixed metal particles by the photoreduction method.

[Claim 2] Said photocatalyst activity corrosion resistance binder is a member which has the photocatalyst operation according to claim 1 characterized by having water repellence.

[Claim 3] Said photocatalyst activity corrosion resistance binder is a member which has the photocatalyst operation according to claim 1 characterized by being a cover coat.

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## DETAILED DESCRIPTION

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[0001]

[Industrial Application] This invention relates to the member which has the function which disassembles harmful matter, such as antibacterial, antifouling property, deodorization nature, and NO<sub>x</sub>, into the front face of base materials, such as a tile, glass (mirror), a sanitary ware, and fancy plywood.

[0002]

[Description of the Prior Art] On the surface of the base material, the approach of forming the thin film of the photocatalyst of anatase TiO<sub>2</sub> grade in a base material front face conventionally is proposed as an approach of adding functions, such as antibacterial, antifouling property, and deodorization nature.

[0003] Anatase mold TiO<sub>2</sub> particle is kneaded to a binder as the one approach, and the approach of applying this to a base material front face, and heat-treating it is learned. As other approaches, these people indicated in JP, 5-253544, A. A binder layer is formed in the front face of the plate-like part material which constitutes the wall surface, floor line, or head-lining side of habitation space. It is made to spray and adhere so that that part may expose to the front face of this binder layer the photocatalyst impalpable powder which makes the anatase mold TiO<sub>2</sub> a subject from a binder layer. Subsequently, after heating in [ 300 degrees-C or more ] less than 900 degrees C and making a binder layer fuse, there is the manufacture approach of the plate-like part material equipped with the deodorization function characterized by cooling and making it make a binder layer solidify.

[0004]

[Problem(s) to be Solved by the Invention] The approach of kneading anatase mold TiO<sub>2</sub> particle to

a binder, and applying this to a base material front face, and heat-treating it was not enough as the property by photocatalyst operation of deodorization nature etc., in order that a binder might cover a site [ activity / photocatalyst ]. Moreover, by the approach of JP,5-253544,A, although deodorization nature etc. was good when heat-treating at 300 degrees C or more less than 900 degrees C, a good deodorization property was not acquired at less than 300-degree C low temperature. Therefore, it was difficult to add photocatalyst activity with the good deodorization property excellent in base materials, such as plastics without thermal resistance, etc. Although it is necessary to carry out mono dispersion of the photocatalyst particle into suspension in the last process which applies a photocatalyst particle to a base material as the reason therefore, the dispersant of an organic system is added, the dispersant does not fully carry out decomposition evaporation at less than 300 degrees C, but it thinks because it remains so that a site [ activity / on a photocatalyst particle ] may be covered.

[0005] Moreover, by the approach of JP,5-253544,A, at the temperature of less than 800 degrees C, the photocatalyst layer which forms a base material front face is the porosity of 40% or more of porosity, therefore there was an inclination for dirt to tends to be attached. Moreover, by the approach of kneading a photocatalyst particle with the resin which has water repellence, and carrying out spreading heat treatment on a base material front face, although it is desirable to have water repellence as for a base material front face if it says from a viewpoint of antibacterial and antifouling property, since a base material front face was covered by the particle which has water repellence further, there was water repellence, but since a site [ activity / on a photocatalyst particle ] will be too covered with water-repellent resin, it did not have photocatalyst activity.

[0006] the member which this invention is made in view of the above situation, and has photocatalyst activity also with good heat treatment of less than 300-degree C low temperature -- producible -- a base material front face -- dirt -- being attached -- hard -- in addition -- and it aims at offering the member structure where other functions, such as photocatalyst activity and water repellence, may be made to live together on a base material front face.

[0007]

[Means for Solving the Problem] In this invention, the thin film which consists of a mixolimnion of the photocatalyst particle and photocatalyst activity corrosion resistance binder which fixed metal particles to the base material front face by the photoreduction method in the member which has a photocatalyst operation that the above-mentioned technical problem should be solved was formed.

[0008] Pottery, a ceramic, a metal, glass, thermosetting resin, thermoplastics, or its composite of the quality of the material of a base material is fundamentally good anything here. What kind of thing is sufficient also as the configuration of a base material, and the thing of the complicated configuration of the thing of the simple configuration of tabular objects, such as a spherical object and cylinder object, a roll, a tile, a wallplate, and flooring, etc. or a sanitary ware, a washstand, an organ bath, a sink, etc. is also available. Moreover, porosity or the substantia compacta is sufficient as a base material front face.

[0009] When it supports to a photocatalyst particle, metal particles mean the metal particles which can catch an electron, when light is irradiated by the photocatalyst particle and an electron and an electron hole generate, and specifically mean Ag, Cu, Pt, Pd, nickel, Co, Fe, etc. The approach of the immobilization by the photoreduction method putting in a photocatalyst particle into a metal salt water solution, irradiating light including ultraviolet rays, and making a metal fixing to a photocatalyst particle is said.

[0010] A photocatalyst particle is a semi-conductor particle which has sufficient band gap to demonstrate a deodorization function, an antibacterial function, etc. Although there is also an opinion (JP,4-29393,B) of carrying out an electrocution by impressing the electrical potential



difference more than predetermined as a reason a photocatalyst particle has an antibacterial function; generally it thinks like the deodorization property for the active oxygen produced at the time of an optical exposure. In order to generate active oxygen, it requires that it is more nearly up than hydrogen generating potential when the location of the conduction band of a semi-conductor expresses with a band scheme, and there is upper limit of a valence band caused from oxygen evolution potential. There are  $\text{TiO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{ZnO}$ ,  $\text{SiC}$ ,  $\text{GaP}$ ,  $\text{CdS}$ ,  $\text{CdSe}$ , and  $\text{MoS}_3$  grade in the semi-conductor which fulfills this condition. Moreover, since the location of a conduction band will be moved up if it atomizes, if it is an about 1-10nm particle,  $\text{SnO}_2$ ,  $\text{WO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Bi}_2\text{O}_3$  grade can also generate active oxygen. Among these, it is chemically stable, and since a particle with cheaply high activity can be obtained, especially the anatase mold  $\text{TiO}_2$  is desirable.

[0011] The production approach of the photocatalyst particle which fixed metal particles by the photoreduction method is performed by the approach shown below. First, a photocatalyst sol solution is produced. If possible, mono dispersion of the photocatalyst sol is carried out. For example, since the isoelectric point is PH6.5, it is made to distribute with acidity or alkalinity in the case of the anatase mold  $\text{TiO}_2$ . Under the present circumstances, in order to raise dispersibility, a dispersant (deflocculant), a surface active agent, or a finishing agent may be added. The solvent used for a photocatalyst sol solution is fundamentally good anything. Generally, water and ethanol are often used.

[0012] Next, the metal solution adjusted to the almost same PH as a photocatalyst sol solution is added in a photocatalyst sol solution. PH of a metal solution is made almost the same as a photocatalyst sol solution for maintaining the mono dispersion nature of a photocatalyst sol here by making it not, change the F-potential in the solution of a photocatalyst sol if possible. The solution which consists of a salt which a metal solution means the solution which consists of a salt containing the metal which can catch an electron when light is irradiated by the photocatalyst particle and an electron and an electron hole generate, and a solvent, and more specifically contains Ag, Cu, Pt, Pd, nickel, Co, Fe, etc., and a solvent here is said. As a salt containing Ag, Cu, Pt, Pd, nickel, Co, Fe, etc., a silver nitrate, copper acetate, copper carbonate, a copper sulfate, a cuprous chloride, a cupric chloride, chloroplatinic acid, a palladium chloride, a nickel chloride, a cobalt chloride, ferrous chloride, a ferric chloride, etc. are mentioned. Moreover, although water, ethanol, propanol, etc. can be used as a solvent, it is desirable to use the class same if possible as a photocatalyst sol.

[0013] Next, light including ultraviolet rays is irradiated, stirring a photocatalyst sol solution and metal salting in liquid. An ultraviolet ray lamp, a BLB lamp, a xenon lamp, a mercury-vapor lamp, a fluorescent lamp, etc. are specifically mentioned that the light source which irradiates the light which includes ultraviolet rays here should just be what may irradiate light including ultraviolet rays. It is better to irradiate in the first place from the container upper part, although the exposure approach of light including ultraviolet rays is not asked fundamentally, either. It is because there is no absorption of ultraviolet rays with a container. Several cm - about 10cm of numbers of the distance of the light source and a container are [ second ] good. It is because an illuminance will fall if too far [ when too near, there is a possibility that the top face of the sample solution may get dry with the heat emitted from the light source, and ]. Although irradiation time changes with illuminances of the light source, if it is irradiated several seconds - about 10 minutes of numbers, a metal will adhere to a photocatalyst particle firmly.

[0014] A photocatalyst activity corrosion resistance binder says the thing of the binder which decomposes and cannot deteriorate easily due to a photocatalysis, and siloxane resin, silicon resin, a fluororesin, a cover coat, silicic-acid glass, etc. are the typical thing. It is better to have translucency, in order for the photocatalyst activity corrosion resistance binder used here to be that

of a wrap about most photocatalyst particles and to make good photocatalyst activity on the front face of a base material into a mixolimnion. In addition, when the point that dirt cannot be attached easily is taken into consideration, as for a binder, what has the water repellence of siloxane resin, a fluoro-resin, etc. is desirable.

[0015]

[Function] Since the site [ activity / particle / photocatalyst ] is beforehand covered by metal particles, such as Ag, Cu, Pt, Pd, nickel, Co, and Fe A site [ activity / particle / photocatalyst ] is not covered with a photocatalyst activity corrosion resistance binder at the time of kneading with a photocatalyst activity corrosion resistance binder. Since many photocatalyst particles are buried into a photocatalyst activity corrosion resistance binder while good photocatalyst activity is maintained according to the supplementary effectiveness of metal particles, when a mixolimnion is formed, A base material front face is comparatively smooth, and dirt cannot be easily attached as compared with the case where the photocatalyst particle is exposed to a base material maximum front face.

[0016]

[Example]

After diluting with propanol the siloxane clearance coat resin which has water repellence in the alumina base material of 10cm angle, (Example 1) Apply the solution which added the curing agent and a nitric acid adjusts PH to the nitric-acid dispersion liquid (PH0.8) of TiO<sub>2</sub> sol of 0.01 micrometers of diameters of a crystal on it further. After having added the copper acetate water solution set to PH 0.8 [ about ], having arranged the light source which becomes the location of about 8cm of solution upper parts from a 4W BLB lamp, and 15 spectra's having irradiated and making TiO<sub>2</sub> support copper, the solid content of TiO<sub>2</sub> sol adds the siloxane clearance coat resin which has water repellence about 20% of the weight, the paint which carried out sequential addition and obtained the propanol and the curing agent of a diluent further is applied, and it heat-treats at 150 degrees C, and is shown in drawing 1 – the sample [ like ] was obtained. In drawing 1, in 1, siloxane clearance coat resin (photocatalyst activity corrosion resistance binder) and 3 show TiO<sub>2</sub> particle (photocatalyst particle), and, as for a base material and 2, 4 shows a copper grain child (metal particles). It evaluated [ sample / which was obtained ] about the deodorization property R30 at the time of an optical exposure (L), and abrasion resistance.

[0017] The deodorization property R30 at the time of an optical exposure (L) is the concentration rate of change after arranging a sample side in distance of 8cm from the light source (BLB fluorescent lamp 4W) in the glassware of 11L, pouring in methyl mercaptan gas into a container so that it may become the initial concentration of 3 ppm, and irradiating 30 spectrum. About abrasion resistance, sliding wear which used the plastics rubber was performed, and change of an appearance was compared and evaluated. A valuation basis is shown below.

O :40 times round trip – receiving – change-less O: – the layer which a blemish enters [ the layer which a blemish enters / the layer which a blemish enters by less than 40 sliding 10 times or more, and contains a photocatalyst / by sliding below more than exfoliation \*\*:5 time 10 time, and contains a photocatalyst ] by sliding below exfoliation x:5 time, and contains a photocatalyst – exfoliation [0018] Consequently, the deodorization property showed the result also with as good abrasion resistance as O R30(L) =80%. As a result of measuring the wetting angle of the water furthermore dropped at the base material front face with the contact angle measuring instrument, it became, the high value was shown and it was checked 73% and that there is water repellence. This high wettability is understood because most base material front faces are covered by water-repellent resin.

[0019] After diluting with propanol the siloxane clearance coat resin which has water repellence in

the alumina base material of 10cm angle, (Example 1 of a comparison) The solution which added the curing agent is applied. Furthermore, the solid content of TiO<sub>2</sub> sol adds on it the siloxane clearance coat resin which has water repellence about 20% of the weight to the nitric-acid dispersion liquid (PH0.8) of TiO<sub>2</sub> sol of 0.01 micrometers of diameters of a crystal, and the paint which carried out sequential addition and obtained the propanol and the curing agent of a diluent further is applied. It heat-treated at 150 degrees C, and the sample was obtained. It evaluated [ sample / which was obtained ] about the deodorization property R30 at the time of an optical exposure (L), and abrasion resistance.

[0020] Consequently, the deodorization property was not good although abrasion resistance indicated the good result to be O, and the deodorization property was carrying out the optical exposure with R30(L) =18%. As a result of measuring the wetting angle of the water furthermore dropped at the base material front face with the contact angle measuring instrument, it became, the high value was shown and it was checked 66% and that there is water repellence. This high wettability is understood because most base material front faces are covered by water-repellent resin.

[0021] A SiO<sub>2</sub>-aluminum<sub>2</sub>O<sub>3</sub>-PbO frit (540 degrees C of softening temperatures) is applied to the tile base material front face of 15cm angle. At 680 degrees C After baking, (Example 2) The light source which adds the copper-sulfate water solution which adjusted PH to the nitric-acid dispersion liquid (PH0.8) of TiO<sub>2</sub> sol of 0.01 micrometers of diameters of a crystal with the nitric acid, and was set to PH 0.8 [ about ], and becomes the location of about 8cm of solution upper parts from a 4W BLB lamp is arranged. The metal support photocatalyst sol which it irradiated [ sol ] 15 spectrum and made TiO<sub>2</sub> support copper, and the kneading object of a SiO<sub>2</sub>-aluminum<sub>2</sub>O<sub>3</sub>-PbO frit were applied, it calcinated at 680 degrees C, and the sample was obtained. It evaluated [ sample / which was obtained ] about the difficulty of being attached of the deodorization property R30 at the time of an optical exposure (L), abrasion resistance, and dirt.

[0022] Evaluation of the difficulty of being attached of dirt drew the line in thick black Magic ink on the base material front face, and evaluated it by dirt condition after wiping off ink by the ethanol after desiccation. An evaluation index is shown.

O : - O: to which marks disappear completely - \*\*:ashes with which marks remain faintly - x: in which blue marks remain - as a result of [ the ] black marks' remaining, R30 (L) was attached 82%, as for abrasion resistance, O and dirt were attached, and the good result was indicated to be hard O.

[0023] (Example 2 of a comparison) After applying a SiO<sub>2</sub>-aluminum<sub>2</sub>O<sub>3</sub>-PbO frit (540 degrees C of softening temperatures) to the tile base material front face of 15cm angle, the nitric-acid dispersion liquid (PH0.8) of TiO<sub>2</sub> sol of 0.01 micrometers of diameters of a crystal were further applied on it, it calcinated at 680 degrees C, and the sample was obtained. It evaluated [ sample / which was obtained ] about the difficulty of being attached of the deodorization property R30 at the time of an optical exposure (L), abrasion resistance, and dirt. Consequently, although R30 (L) showed the result with as good abrasion resistance as O 92%, the difficulty of being attached of dirt was x.

[0024]

[Effect of the Invention] the member which has photocatalyst activity also with good heat treatment of less than 300-degree C low temperature by forming in the base material front face the thin film which consists of a mixolimnion of the photocatalyst particle and photocatalyst activity corrosion resistance binder which fixed metal particles by the photoreduction method - producible - a base material front face - dirt - being attached - hard - abrasion resistance - good - in addition - and the member structure where other functions, such as photocatalyst activity and water repellence,

may be made to live together on a base material front face can be offered.

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## CLAIMS

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[Claim 1] TiO<sub>2</sub> whose particle size is 5-300nm from – the compound ultrafine particle which an ultrafine particle with a particle size [ of a minor diameter ] of 0.5-50nm projects from this on the becoming ultrafine particle front face, and it comes to support – it is – the above TiO<sub>2</sub> an ultrafine particle – anatase mold TiO<sub>2</sub> Rutile mold TiO<sub>2</sub> TiO<sub>2</sub> characterized by including an ultrafine particle System compound ultrafine particle.

[Claim 2] TiO<sub>2</sub> according to claim 1 which are at least one sort of metals chosen from the group which the ultrafine particle supported becomes from Fe, Co, nickel, Cu, Ru, Rh, Pd, Ag, Pt, and Au, or/and its compound (the ceramics is included) System compound ultrafine particle.

[Claim 3] TiO<sub>2</sub> from – the becoming ultrafine particle – anatase mold TiO<sub>2</sub> 50 - 80 % of the weight of ultrafine particles, and rutile mold TiO<sub>2</sub> TiO<sub>2</sub> according to claim 1 or 2 which consists of 20 - 50 % of the weight of ultrafine particles System compound ultrafine particle.

[Claim 4] general formula Ti-M (it Rh(s) however, M – Fe, Co, nickel, Cu, and Ru –) they are at least one sort of elements chosen from the group which consists of Pd, Ag, Pt, and Au. The inside of the gas ambient atmosphere which contains oxygen or/and nitrogen for the raw material which consists of a presentation shown, [ whether the heating dissolution is carried out in an inert gas ambient atmosphere or nitrogen-gas-atmosphere mind, and the raw material which evaporated is made to react with the oxygen in the above-mentioned ambient atmosphere, and ] or it reacts with oxygen after ultrafine particle generation – making – TiO<sub>2</sub> from – TiO<sub>2</sub> characterized by producing the compound ultrafine particle which the ultrafine particle of a minor diameter projects from this on the becoming ultrafine particle front face, and it comes to support The manufacture approach of a system compound ultrafine particle.

[Claim 5] The approach according to claim 4 using the alloy which consists of Ti50 - 99 atom %, and one to M element 50 atom % as a raw material.

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## DETAILED DESCRIPTION

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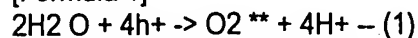
[0001]

[Industrial Application] this invention – TiO<sub>2</sub> a system compound ultrafine particle and its manufacture approach – being related – further – detailed – TiO<sub>2</sub> from – TiO<sub>2</sub> which the ultrafine particle of a minor diameter projects from this on the becoming ultrafine particle front face, and it comes to support It is related with a system compound ultrafine particle and its manufacture approach.

[0002]

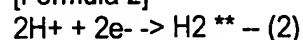
[Description of the Prior Art] TiO<sub>2</sub> It is known that it is very effective as a photocatalyst. For example, if a semi-conductor (TiO<sub>2</sub>) electrode and a platinum electrode are immersed underwater and light is irradiated, in a semiconductor electrode, the electron (e<sup>-</sup>) which suited the valence band will be excited by the conduction band, and an electron hole (h<sup>+</sup>) will generate to a valence band. Consequently, h<sup>+</sup> produced in the valence band It moves to a semiconductor electrode front face, and reacts with water according to the reaction formula (1) of the following-izing 1, and oxygen occurs from the front face of a semiconductor electrode.

[Formula 1]



[0003] On the other hand, from the interior of a semiconductor electrode, the excitation electron (e<sup>-</sup>) produced in the conduction band reaches a platinum electrode through lead wire, returns a proton (H<sup>+</sup>) like the reaction formula (2) of the following-izing 2 here, and generates hydrogen.

[Formula 2]



The decomposition reaction of the water by such semiconductor electrode is called Honda and the Fujishima effectiveness.

[0004] Although research on a semi-conductor photoelectrical pole has been advanced all over the world by doing the beginning Honda's and Fujishima's and others research, it is found out instead of using a semiconductor electrode that the decomposition reaction of water occurs also with the photocatalyst which made noble metals, such as Pt and Ru, adhere on semi-conductor powder. This principle is the same as that of electrode reaction, and it is thought here that Pt which adhered on semi-conductor powder carries out the duty of a cathode. as a semi-conductor – the above TiO<sub>2</sub> others – SrTiO<sub>3</sub> etc. is used (strontium titanate). Disassembling alcohol and the organic substance more easily is also known rather than such a photocatalyst disassembles water. moreover, TiO<sub>2</sub> etc. – it is indicated by JP,4-29393,B that the powder which made semi-conductor powder or this support Pt etc. has a killer cell operation to various microorganisms, tumor cells, etc., such as bacteria, an Actinomyces, mold, algae, and yeast. furthermore, TiO<sub>2</sub> etc. – a photocatalyst has the deodorization effectiveness – JP,4-307066,A – moreover, OH radical generated when these receive an optical exposure in the condition of touching with the moisture in the oral cavity is made to generate dental plaque disintegration or a dental plaque – a disease germ – it is indicated by JP,3-20363,B that the germicidal action to a mu factor wardrobe bacillus is shown.

[0005] It is TiO<sub>2</sub> as mentioned above. It is the rutile mold TiO<sub>2</sub> obtained by JP,2-6333,A by carrying out vapor-phase-oxidation decomposition of the titanium tetrachloride, for example as the manufacture approach of the powder which adhered the metal on the surface of the particle. It is TiO<sub>2</sub> by being first immersed into a stannous chloride water solution, and subsequently to the inside of a palladium-chloride water solution immersing powder. The method of making palladium adhere to a particle front face is indicated. Moreover, said JP,3-20363,B is made to suspend semi-conductor powder in a chloroplatinic acid water solution, and the optical electrocrystallization method for depositing platinum on a semi-conductor and the kneading method which kneads semi-conductor powder with platinum black are proposed by carrying out an optical exposure under nitrogen-gas-atmosphere mind.

[0006]

[Problem(s) to be Solved by the Invention] It is TiO<sub>2</sub> as described above. It is very effective as a photocatalyst. especially the compound ultrafine particle that supported ultrafine particles, such as a metal and its oxide, on the front face of TiO<sub>2</sub> ultrafine particle discovers said catalyst property of

versatility which was carried out -- high -- it is expectable as an activity photocatalyst. The former and TiO<sub>2</sub> The powder which made the metal etc. adhere to a particle front face is produced mainly by the liquid phase process, as described above. However, in order to produce in a liquid, the component contained in the liquid remains as an impurity into powder, and there is a problem that the activity as a catalyst will become low by it. although it is necessary to raise powdered purity in order to acquire the catalyst of high activity especially, or the correspondence is difficult in the case of a liquid phase process -- or a production process -- complicated -- cost -- it will become quantity: [0007] Moreover, in the case of a well-known liquid phase process, it is TiO<sub>2</sub> conventionally. A metal is made to adhere to a TiO<sub>2</sub> particle front face by powdered chemical preparation. TiO<sub>2</sub> To generation and coincidence of an ultrafine particle, it is TiO<sub>2</sub>. Producing the compound ultrafine particle of nm order which supported ultrafine particles, such as a metal and its oxide, on the surface of the ultrafine particle at one step of process by the gaseous-phase method is not conventionally known, as far as this invention persons get to know. Furthermore, TiO<sub>2</sub> of the anatase mold marketed Since powder is produced at low temperature as compared with a rutile mold, generally in the liquid phase process with them, TiO<sub>2</sub> powder of a rutile mold with few impurities than an anatase mold is used as a start ingredient (refer to above-shown JP,2-6333,A). [ there are many impurities, therefore conventionally well-known ] However, on the other hand, it is TiO<sub>2</sub> of a rutile mold. Powder has the difficulty that the activity of a photocatalyst is low as compared with an anatase mold.

[0008] Therefore, the fundamental purpose of this invention is TiO<sub>2</sub>. It is in offering the compound ultrafine particle of nm order which supported ultrafine particles, such as a metal and its oxide, on the surface of the ultrafine particle. Furthermore, the purpose of this invention is TiO<sub>2</sub> which supports ultrafine particles, such as a metal and its oxide. An ultrafine particle is TiO<sub>2</sub> of both an anatase mold and a rutile mold. It is in offering the high activity which may discover various photocatalyst properties which were described above by the light of a comparatively wide range wavelength region, and the compound ultrafine particle of a high grade including an ultrafine particle. Other purposes of this invention are to offer the approach that the above compound ultrafine particles can be manufactured comparatively easily at one step of process by the gaseous-phase method.

[0009]

[Means for Solving the Problem] TiO<sub>2</sub> whose particle size is 5-300nm according to this invention in order to attain said purpose from -- the compound ultrafine particle which an ultrafine particle with a particle size [ of a minor diameter ] of 0.5-50nm projects from this on the becoming ultrafine particle front face, and it comes to support -- it is -- the above TiO<sub>2</sub> an ultrafine particle -- anatase mold TiO<sub>2</sub> Rutile mold TiO<sub>2</sub> The TiO<sub>2</sub> system compound ultrafine particle characterized by including an ultrafine particle is offered. In a suitable mode, said ultrafine particles supported are at least one sort of metals chosen from the group which consists of Fe, Co, nickel, Cu, Ru, Rh, Pd, Ag, Pt, and Au, or/and a compound (the ceramics is included) of those.

[0010] Furthermore, according to this invention, the approach for manufacturing the above compound ultrafine particles is also offered. The approach General formula Ti-M (however, M is at least one sort of elements chosen from the group which consists of Fe, Co, nickel, Cu, Ru, Rh, Pd, Ag, Pt, and Au.) The inside of the gas ambient atmosphere which contains oxygen or/and nitrogen for the raw material which consists of a presentation shown, [ whether the heating dissolution is carried out in an inert gas ambient atmosphere or nitrogen-gas-atmosphere mind, and the raw material which evaporated is made to react with the oxygen in the above-mentioned ambient atmosphere, and ] or it reacts with oxygen after ultrafine particle generation -- making -- TiO<sub>2</sub> from -- it is characterized by producing the compound ultrafine particle which the ultrafine particle of a

minor diameter projects and it comes to support from this on the becoming ultrafine particle front face. In a suitable mode, the alloy which consists of Ti50 - 99 atom %, and one to M element 50 atom % as the above-mentioned raw material is used.

[0011]

[Function and Embodiment of the Invention] That this invention persons should attain said purpose, wholeheartedly, in case an alloy is fused with an arc etc. and an ultrafine particle is manufactured as a result of research, while using the gas ambient atmosphere which contains oxygen or/and nitrogen as the ambient atmosphere, an inert gas ambient atmosphere, or nitrogen-gas-atmosphere mind If the alloy of the presentation shown by general formula Ti-M (M=Fe, Co, nickel, Cu, Ru, Rh, Pd, Ag and Pt, or Au) is used as a hardener which dissolves with an arc etc., as shown in drawing 1 TiO<sub>2</sub> from – it found out that the detailed compound ultrafine particle of nm level of the structure which ultrafine particles, such as a metal (M) of a minor diameter and its oxide (M-O), joined to the becoming ultrafine particle front face from this was produced. In this case, each TiO<sub>2</sub> An ultrafine particle is the anatase mold TiO<sub>2</sub>. An ultrafine particle or rutile mold TiO<sub>2</sub> Although it consists of either of the ultrafine particles, it is TiO<sub>2</sub> of both molds. An ultrafine particle generates. namely, the compound ultrafine particle produced – overall – a support particle (big particle of the path which is supporting the particle of a minor diameter) – TiO<sub>2</sub> of an anatase mold from – TiO<sub>2</sub> of the becoming compound ultrafine particle and rutile mold from – it consists of becoming mixture of a compound ultrafine particle. Each TiO<sub>2</sub> [ on the other hand ] The ultrafine particles of a minor diameter are only a metal (M) and its oxide, or a metal and its oxide are mixed and they exist rather than it is supported by the ultrafine particle.

[0012] When the gas (inert gas or nitrogen gas) ambient atmosphere which contains oxygen as a controlled atmosphere is used, the compound ultrafine particle of the structure described above in the ultrafine particle generation process is produced. On the other hand, since the ultrafine particle generated in the ultrafine particle generation process does not serve as an oxide system when a controlled atmosphere does not contain oxygen, it is necessary to make it react with oxygen after that, and to change into an oxide system. Since the compound ultrafine particle of the structure which supported two or more M metal particles of a minor diameter more by the TiN particle generates when only nitrogen gas is used as a controlled atmosphere, it heat-treats and oxidizes in an oxygen ambient atmosphere (for example, atmospheric air) after that. By it, it is TiO<sub>2</sub>. The compound ultrafine particle of the structure which the metal (M) and its oxide (M-O) of a minor diameter joined on the surface of [ this ] the ultrafine particle is obtained.



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## CLAIMS

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[Claim 1] The member which the layer which consists of a particle which mainly has photocatalyst activity is formed on a base material, and has the photocatalyst function characterized by carrying out distributed combination of the particle with a mean particle diameter of less than 0.01 micrometers in said particle layer.

[Claim 2] The member which is a member which has a photocatalyst function according to claim 1, and has the photocatalyst function characterized by carrying out distributed combination of the particle with a mean particle diameter of less than 0.01 micrometers 15% of the weight or more to the whole layer in said particle layer.

[Claim 3] The member which has the photocatalyst function which the layer which consists of a particle which mainly has photocatalyst activity with a mean particle diameter of 0.02 micrometers or less is formed on a base material, and is characterized by the thing of said particle layer done at the maximum surface section for the distributed combination of the particle with a mean particle diameter of less than 0.01 micrometers at least.

[Claim 4] The member which has the photocatalyst function which is the member which has a photocatalyst function according to claim 3, and is characterized by the thing of said particle layer done 15% of the weight or more to the whole layer at the maximum surface section for the distributed combination of the particle with a mean particle diameter of less than 0.01 micrometers at least.

[Claim 5] The manufacture approach of a member of having the photocatalyst function characterized by applying and calcigating the particle which has the photocatalyst activity which blended the particle with a mean particle diameter of less than 0.01 micrometers on the base material.

[Claim 6] The manufacture approach of a member of having the photocatalyst function characterized by applying and calcinating a particle with a mean particle diameter of less than 0.01 micrometers after applying the particle which has photocatalyst activity on a base material.

[Claim 7] The manufacture approach of a member of having the photocatalyst function characterized by applying and fixing a particle with a mean particle diameter of less than 0.01 micrometers after applying the particle layer which has photocatalyst activity on a base material and performing the process to calcinate.

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## DETAILED DESCRIPTION

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[0001]

[Industrial Application] This invention relates to the member in which the layer which has photocatalyst functions, such as antibacterial, deodorization, and antifouling, was formed on front faces, such as a tile, glass (mirror), a sanitary ware, building materials, or a resin plate, and its manufacture approach.

[0002]

[Description of the Prior Art] The approach of forming in a base material front face conventionally the thin film which consists of matter which has photocatalyst activity, such as anatase mold titanium oxide, on the surface of a base material as an approach of adding functions, such as antibacterial, antifouling property, and deodorization nature, is proposed.

[0003] An anatase mold titanium oxide particle is kneaded to a binder as the one approach, and the approach of applying this to a base material front face, and heat-treating it is learned.

[0004] As other approaches, these people indicated in JP,5-253544,A. A binder layer is formed in the front face of the plate-like part material which constitutes the wall surface, floor line, or head-lining side of habitation space. It is made to spray and adhere so that that part may expose to the front face of this binder layer the photocatalyst impalpable powder which makes anatase mold titanium oxide a subject from a binder layer. Subsequently, after heating in [ 300 degrees-C or more ] less than 900 degrees C and making a binder layer fuse, there is the manufacture approach of the plate-like part material equipped with the deodorization function characterized by cooling and making it make a binder layer solidify.

[0005]

[Problem(s) to be Solved by the Invention] The approach of kneading an anatase mold titanium oxide particle to a binder, and applying this to a base material front face, and heat-treating it was not enough as the property based on photocatalyst activity, such as deodorization, in order that a binder might cover a site [ activity / photocatalyst ].

[0006] Moreover, although other photocatalyst properties, such as an antibacterial function, were good besides the deodorization function when manufactured by the approach of JP,5-253544,A in [ 300 degrees-C or more ] less than 900 degrees C, film reinforcement was weak and especially less than 800 degrees C of abrasion resistance that solid phase sintering of titanium oxide particles does not produce were not enough. On the other hand, above 900 degrees C which solid phase sintering fully produces, anatase mold titanium oxide carried out phase transition to the rutile type titanium dioxide with low activity, and sufficient photocatalyst activity was not acquired.

[0007] It aimed at offering the member which has sufficient film reinforcement, this invention having been made in view of the above situation, and maintaining photocatalyst activity.

[0008]

[Problem(s) to be Solved by the Invention] In this invention, the layer which consists of a particle which mainly has photocatalyst activity is formed on a base material that the above-mentioned technical problem should be solved, and the distributed combination of the particle with a mean particle diameter of less than 0.01 micrometers was made to be carried out at said particle layer. Or the layer which consists of a particle which mainly has photocatalyst activity with a mean particle diameter of 0.02 micrometers or less was formed on the base material, and even if there

were few said particle layers, the distributed combination of the particle with a mean particle diameter of less than 0.01 micrometers was made to be carried out at the maximum surface section.

[0009] A ceramic, a pottery ingredient, a metal, glass, thermosetting resin, thermoplastics, or those composites of the quality of the material of a base material are fundamentally good anything here. What kind of thing is fundamentally sufficient also as the configuration of a base material, for example, the thing of the complicated configuration of the accessory etc. is also available for the thing of the simple configuration of a tabular objects and cylindrical objects, spherical object, cylindrical object, cylindrical object, and prismatic form object, a prismatic form object in the air, etc. or a sanitary ware, a washstand, an organ bath, a sink, etc. [, such as a tile, a wallplate, and flooring, ]

[0010] The particle layer which has photocatalyst activity is the semantics of the layer which consists of a particle which mainly has photocatalyst activity. Therefore, any matter other than the particle which has photocatalyst activity in this layer does not care about little \*\* rare \*\*\*\*\* , either. As such matter, the matter which has the electron capture effectiveness, such as silver, copper, platinum, palladium, gold, iron, nickel, cobalt, zinc, and a cuprous oxide, for example is mentioned. If the matter which has these electron capture effectiveness is contained, photocatalyst activity will improve more.

[0011] The particle which has photocatalyst activity is a semi-conductor particle which has sufficient band cap to demonstrate photocatalyst functions, such as an antibacterial function and a deodorization function. Although there is also an opinion (JP,4-29393,B) of carrying out an electrocution by impressing the electrical potential difference more than predetermined as a reason a photocatalyst particle has antibacterial, generally it thinks like the deodorization function for the active oxygen produced at the time of an optical exposure. In order to generate active oxygen, it requires that it is more nearly up than hydrogen generating potential when the location of the conduction band of a semi-conductor expresses with a band scheme, and there is upper limit of a valence band caudad from oxygen evolution potential. There are titanium oxide, strontium titanate, a zinc oxide, silicon carbide, gallium phosphide, a cadmium sulfide, a cadmium selenide, 3 molybdenum sulfides, etc. in the semi-conductor which fulfills this condition. Moreover, since the location of a conduction band will be moved up if it atomizes, if it is an about 1-10nm particle, the tin oxide, a tungstic trioxide, ferric oxide, bismuth(III) oxide, etc. can generate active oxygen. Among these, it is chemically stable, and since a particle with cheaply high activity can be obtained, especially anatase mold titanium oxide is desirable.

[0012] Moreover, the maximum surface part of the base material which can be observed with an electron microscope as the maximum surface section of the layer which consists of a particle which has photocatalyst activity is shown. One of the examples is shown in drawing 1 . The layer which consists of a particle which mainly has photocatalyst activity consists of the particle 1 and the particle 2 with a mean particle diameter of less than 0.01 micrometers which have photocatalyst activity. Since a particle 2 is constituted by the ultrafine particle with a mean particle diameter of less than 0.01 micrometers, it has big surface energy and curved-surface energy. Therefore, particle 1 comrades are mutually combined by these potential energy that a particle 2 has. Or neck association with the insufficient particles which have photocatalyst activity is complemented. When the particle 2 is constituted by the matter which has photocatalyst activity, it is still more desirable here. Moreover, as shown in drawing 1 , when the particle 2 distributes and exists in homogeneity over the whole particle layer which has photocatalyst activity, it is more desirable.

[0013] When a particle 2 exists only in the maximum surface section like drawing 2 , it is necessary to compensate with other approaches association of the particles inside the particle layer which

has photocatalyst activity. It is good as for 0.02 micrometers or less in the mean particle diameter of the particle inside the particle layer which has photocatalyst activity as the approach. Wear understands thing with the mean particle diameter of the particle inside a particle layer sufficient with 0.02-micrometer or less extent because being generated from the maximum surface and transfer of the shearing force which joins the maximum surface section are eased inside to the thing whose particle with a mean particle diameter of less than 0.01 micrometers is the need in the maximum surface section here. Moreover, as other approaches, burning temperature may be raised to about 800 degrees C, and neck section association may be formed. However, this approach is restricted when adding a particle with a mean particle diameter of less than 0.01 micrometers after baking. It is because a particle will also carry out grain growth if it is made 800 degrees C or more.

[0014] Moreover, in drawing 1 and 2, between a base material and the particle layers which have photocatalyst activity is considered that association is made by the above-mentioned potential energy. Since transfer of the shearing force which joins producing wear from the maximum surface and the maximum surface section is eased inside also in this part, association to that extent is fundamentally enough. Moreover, in the member which has this photocatalyst activity, binders, such as a cover coat and an inorganic vitreous material, may be minded between a base material and the particle layer which has photocatalyst activity. It is because affinity with a base material improves more.

[0015]

[Function] Since the filling factor of the maximum surface section is raised and photocatalysts come to be mutually combined by potential energy through a particle with a mean particle diameter of less than 0.01 micrometers by [ of the particle layer which has photocatalyst activity ] the distributed combination of the particle with a mean particle diameter of less than 0.01 micrometers being made to be carried out at least at the maximum surface section, overall film reinforcement is raised and it becomes possible to demonstrate sufficient abrasion resistance.

[0016]

[Example] Next, the manufacture approach of a member of having the above-mentioned photocatalyst activity is explained. The approach applies the particle which has the photocatalyst activity by which the particle with a mean particle diameter of less than 0.01 micrometers was blended for example, on the base material. The approach of calcinating, and the method of applying and calcinating a particle with a mean particle diameter of less than 0.01 micrometers after applying the particle layer which has photocatalyst activity on a base material, After applying the particle layer which has photocatalyst activity on a base material and performing the process to calcinate, a particle with a mean particle diameter of less than 0.01 micrometers is applied, and is performed by the approach of fixing.

[0017] The particle which has the photocatalyst activity by which the particle with a mean particle diameter of less than 0.01 micrometers was first blended on the base material is applied, and how to calcinate is explained. A particle with a mean particle diameter of less than 0.01 micrometers is mixed to the particle which has photocatalyst activity first in this approach. It is better to make it have as big a filling factor as possible, where the smaller one of the porosity of the member finally obtained was good here, therefore this mixture is applied. It is better to blend a particle with a mean particle diameter of less than 0.01 micrometers and a larger particle than it for that purpose. However, it is better for said large particle to be 0.02 micrometers or less at the time of spreading at least, if adhesion with a base material is taken into consideration. Since the effectiveness by particle size blending shows up notably in case of twice [ more than ] the particle with a mean particle diameter of less than 0.01 micrometers, said large particle is desirable. Moreover, as for a

particle with a mean particle diameter of less than 0.01 micrometers, consisting of matter which has photocatalyst activity is desirable.

[0018] The approach of forming the particle layer which has photocatalyst activity on a base material is performed by applying the above-mentioned compound to a base material. In this case, when the above-mentioned compound is applied as sol suspension, it is desirable from being easy to apply to homogeneity and being easy to control particle size. Moreover, since the method of application tends to control that there are few amounts of the solution to be used and they end, and thickness, its spray coating method is desirable.

[0019] The approach of fixing to a base material is performed heat-treating at the low temperature which is extent in which the applied particle does not carry out grain growth notably, and by heat-treating at less than 800 degrees C preferably, making a particle with a mean particle diameter of less than 0.01 micrometers remain.

[0020] Next, how to apply and calcinate a particle with a mean particle diameter of less than 0.01 micrometers is explained after applying the particle layer which has photocatalyst activity on a base material. The approach of applying the particle layer which has photocatalyst activity on a base material is desirable from being easy to apply applying the sol suspension which has photocatalyst activity to homogeneity, and tending to control particle size. Moreover, it is more desirable from a viewpoint of adhesion with a base material for the mean particle diameter of the sol which has photocatalyst activity to be 0.02 micrometers or less. Moreover, since the method of application tends to control that there are few amounts of the solution to be used and they end, and thickness, its spray coating method is desirable.

[0021] Then, before applying a particle with a mean particle diameter of less than 0.01 micrometers, said spreading object may be dried. A particle with a mean particle diameter of less than 0.01 micrometers becomes easy to enter the gap of the particle which has photocatalyst activity by doing so.

[0022] The approach of applying a particle with a mean particle diameter of less than 0.01 micrometers is also desirable from being easy to apply applying the sol suspension of a particle with a mean particle diameter of less than 0.01 micrometers to homogeneity, and tending to control particle size. As for a particle with a mean particle diameter of less than 0.01 micrometers, consisting of matter which has photocatalyst activity is desirable.

[0023] The adhesion over a base material can be improved by calcinating after that. The temperature is performed heat-treating at the low temperature which is extent in which the applied particle does not carry out grain growth notably, and by heat-treating at less than 800 degrees C preferably.

[0024] (Example 1) Specified quantity mixing of the ammonia amalgam-decomposition mold suspension of the titanium oxide sol of 0.004 micrometers of mean diameters was carried out at the ammonia amalgam-decomposition mold suspension of the titanium oxide sol of 0.01 micrometers of mean diameters, and it calcinated at 750 degrees C after spreading with the spray coating method to the tile substrate of 15cm angle. At this time, the mean diameter of the titanium oxide sol in titanium oxide sol additive-free [ of 0.004 micrometers of mean diameters ] was 0.04 micrometers. About the obtained sample, abrasion resistance, the deodorization property, and the antibacterial property were evaluated.

[0025] Abrasion resistance performed sliding wear which used the plastics rubber, and compared and evaluated change of an appearance. An evaluation index is shown below.

O with no change to :40 times round trip – sliding below more than O:10 time 40 time – a blemish -  
- entering – a titanium oxide layer – sliding below more than exfoliation \*\*:5 time 10 time – a blemish – entering – a titanium oxide layer – sliding below exfoliation x:5 time – a blemish –

entering -- a titanium oxide layer -- exfoliation [0026] The deodorization property was evaluated by measuring R30 (L). R30 (L) be an elimination factor after an optical exposure, the field which specifically formed the particle layer which have the photocatalyst activity of a sample in the glassware of 11L be arrange in distance of 8cm from the light source (BLB fluorescent lamp 4W), and it pour in into a container and be obtain by measure the concentration change when carry out an optical exposure for 30 minutes so that it may become the initial concentration of 3 ppm about methyl mercaptan gas.

[0027] The antibacterial property was examined using Escherichia coli (Escherichia coli W3110 share). The glass plate (100x100) which trickled 0.15ml (10000-50000CFU) of fungus liquid was stuck to the field in which the particle layer which has the photocatalyst activity of the member beforehand sterilized by ethanol 70% was formed, and it considered as the sample. The fungus liquid of the sample which irradiated the white LGT (3500 luxs) after the exposure for 30 minutes was wiped with sterile absorbent gauze; it collected to 10ml of physiological salines, the survival rate of a bacillus was searched for, and it considered as the index of evaluation. An evaluation index is shown below.

+ ++ : 10% [ of below survival rates ] ++ of Escherichia coli : Below 10% or more survival rate [ of Escherichia coli / 30% ] + : Less than 70% of 30% or more survival rates of Escherichia coli - : 70% or more of survival rates of Escherichia coli [0028] Consequently, about the deodorization property, even if the amount of the titanium oxide sol of 0.004 micrometers of mean diameters was any, the good result was indicated to be 90% or more. Moreover, also about the antibacterial property, even if the amount of the titanium oxide sol of 0.004 micrometers of mean diameters was any, the good result was indicated to be +++. About abrasion resistance, change was accepted with the amount of the titanium oxide sol of 0.004 micrometers of mean diameters, and it became O at 15 % of the weight or more that it was x at 10 or less % of the weight.

[0029] (Example 2) After applying the ammonia amalgam-decomposition mold suspension of the titanium oxide sol of 0.01 micrometers of mean diameters to the tile substrate of 15cm angle with the spray coating method and drying, specified quantity spreading of the ammonia amalgam-decomposition mold suspension of the titanium oxide sol of 0.004 micrometers of mean diameters was carried out with the spray coating method, and it calcinated at 750 degrees C. At this time, the mean diameter of the titanium oxide sol in titanium oxide sol additive-free [ of 0.004 micrometers of mean diameters ] was 0.04 micrometers. About the obtained sample, abrasion resistance, the deodorization property, and the antibacterial property were evaluated.

[0030] Consequently, about the deodorization property, even if the amount of the titanium oxide sol of 0.004 micrometers of mean diameters was any, the good result was indicated to be 90% or more. Moreover, also about the antibacterial property, even if the amount of the titanium oxide sol of 0.004 micrometers of mean diameters was any, the good result was indicated to be +++. About abrasion resistance, change was accepted with the amount of the titanium oxide sol of 0.004 micrometers of mean diameters, and it became O at 15 % of the weight or more that it was x at 10 or less % of the weight.

[0031] (Example 3) The ammonia amalgam-decomposition mold suspension of the titanium oxide sol of 0.01 micrometers of mean diameters was calcinated at 850 degrees C. after spreading with the spray coating method to the tile substrate of 15cm angle. The crystal mold of the titanium oxide at this time was an anatase mold, that mean particle diameter is 0.1 micrometers, and the neck section was observed between particles. Specified quantity spreading of the ammonia amalgam-decomposition mold suspension of the titanium oxide sol of 0.004 micrometers of mean diameters was carried out with the spray coating method after that, it calcinated and fixed at 11.0 degree C, and the sample was obtained. About the obtained sample, abrasion resistance, the deodorization

property, and the antibacterial property were evaluated.

[0032] Consequently, about the deodorization property, even if the amount of the titanium oxide sol of 0.004 micrometers of mean diameters was any, the good result was indicated to be 80% or more. Moreover, also about the antibacterial property, even if the amount of the titanium oxide sol of 0.004 micrometers of mean diameters was any, the good result was indicated to be ++ - +++.

About abrasion resistance, change was accepted with the amount of the titanium oxide sol of 0.004 micrometers of mean diameters, and it became O at 15 % of the weight or more that it was O at 10 or less % of the weight.

[0033]

[Effect of the Invention] The layer which consists of a particle which mainly has photocatalyst activity is formed on a base material, and in said particle layer [ whether the distributed combination of the particle with a mean particle diameter of less than 0.01 micrometers is made to be carried out, and ] The layer which consists of a particle which mainly has photocatalyst activity with a mean particle diameter of 0.02 micrometers or less is formed on a base material. Or by [ of said particle layer ] the distributed combination of the particle with a mean particle diameter of less than 0.01 micrometers being made to be carried out at least at the maximum surface section Sufficient film reinforcement is obtained maintaining photocatalyst activity.